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ORIGINAL ARTICLE

Assessment of agricultural crops and natural vegetation in Scotland for energy production by anaerobic digestion and hydrothermal liquefaction

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Abstract The current paper investigates the use of natural vegetation and agricultural crops commonly found in Scotland as a source of bioenergy. Such biomass is shown to have a high moisture content upon harvest (~80%) which renders them suitable for wet conversion technologies such as anaerobic digestion (AD) and hydrothermal liquefaction (HTL). Experimental investigations are carried out on 16 different types of biomass to assess their bio-crude yields via HTL and theoretical methane potential via AD based on compositional analysis. The different types of biomass vary significantly in biomass yield upon harvesting from 1.1 t/ha (dry matter) for bracken to a maximum of 17.5 t/ha for winter rye. These area specific yields are the most influential factor in the final energy yield per area. Area specific energy yields are found to average at 67 GJ/ha for AD and 53 GJ/ha for HTL. The respective conversion efficiencies of HTL and AD for different biomass feedstocks are also shown to be an important factor on the overall energy potential. AD averages a mass to energy conversion of 9.1 GJ/t compared to 7.2 GJ/t for HTL. A combination of AD and HTL is investigated by liquefying digestate from rye, but the results suggest this is not a viable option due to low bio-crude yields. However, analysis of the water phase post HTL allowed the calculation of theoretical methane potential from the HTL process water and suggests that this can yield additional energy. Overall, the work shows that utilisation of natural vegetation is a promising approach for bioenergy production.

Keywords Hydrothermal liquefaction · Grass · Natural vegetation · Anaerobic digestion · Bio-crude · Crops

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1 Introduction

There has been an increasing use of high yielding agricultural crops for renewable energy production through anaerobic digestion to methane gas. In the UK, this has been largely due to government incentives from the Renewable Heat Initiative and Feed in Tariff subsidy. Commonly used crops include forage maize, winter rye and energy beet, all of which produce large amounts of biomass per unit area [1]. However, concerns about using good quality agricultural land for energy production have led to an increasing interest in the potential for crops and forage grasses that will grow on more marginal land or indeed the use of harvestable natural vegetation, such as bracken, for energy production [2].

Methane production by anaerobic digestion provides a number of potential energy outputs: biogas for heating, combined heat and power (CHP) to produce electricity, direct injection of methane to grid or compression to provide a vehicle fuel. This flexibility and the potential for crop growth on marginal, less fertile soils could make anaerobic digestion (AD) technology particularly suitable for more remote areas of Scotland where access to energy for heating, electricity and transport can be problematic and expensive. However, there are disadvantages with AD systems particularly with regard to the storage and transport of the biogas or methane gas output.

One alternative means of producing energy from such crops and vegetation is through the process of hydrothermal liquefaction (HTL). By applying high temperature and pressure to aqueous biomass slurries, biomass is converted to a bio-crude which can be used for combustion or processed to produce transport fuels after hydrotreating. Although the technology is not as mature as AD, it does have particular advantages which may be of value for remote communities where oil is used for heating purposes, and the potential exists to grow crops and harvest vegetation for bio-crude production. One particular advantage would be ease of storage of the bio-crude product as compared to the biogas produced from AD.

Hydrothermal liquefaction has predominantly been investigated for the production of bio-crude from aquatic biomass such as micro- and macroalgae. The utilisation of perennial grasses and natural vegetation is very limited in the literature. Switchgrass, barley straw and miscanthus have been processed via HTL [3–5], and barley straw showed promising results with bio-crude yields of around 35% and energy recovery of around 55%. Apart from these two studies, there is a distinct lack in the literature into the investigation of agricultural crops and forage grasses.

The current investigation was established to process a range of 16 different biomass materials by HTL to assess the potential energy yields and compare them to anaerobic digestion. In addition, tests are carried out on production of bio-crude material produced from the residual digestate after commercial AD of feedstock composed primarily of winter rye. A combination of the two technologies is evaluated by calculating the methane potential of the HTL aqueous phase and discussed in terms of water phase composition. The current study presents the most in depth assessment of a broad range of agricultural crops and forage grasses for bioenergy production via AD and HTL to date.

2 Materials and methods

Biomass was collected by a variety of harvesting methods including Softrak tracked flail mower, hand shears, Haldrup plot mower and manually. The harvest locations, names and harvest dates are listed in Table 1 for the 16 different biomass samples plus the digestate from AD.

Materials from plots at all sites were weighed after harvesting. Samples were then weighed and dried at 100 °C for 4 h in a forced draught oven and re-weighed for dry matter content. For the cereals, two replicate samples were measured and bulked for subsequent energy analysis.

A subsample of dried material was sent to the Scottish Rural College's Analytical Services Department (SRUC ASD) Laboratories, Penicuik (Scotland), for biological methane potential by analysis of: crude fibre, crude protein, acid hydrolysed ether extract for oil content and ash content. Analysis was not carried out on the material from herb-dominated pasture and bog myrtle due to insufficient sample size. The methane potential was calculated from each component and then totalled for whole crop methane potential using the equations described by Keymer and Schilcher (2003) [6]. These take into account the digestibility of the components (from animal nutrition trials) along with their methane productivity as shown in Table 2. In terms of plant dry matter, methane productivity is calculated from the following:

Table 1 Summary of biomass and harvesting location and date

Biomass source	Location[a]	Harvest date
Herb-dominated pasture	A	06/10/2014
Bog myrtle	A	11/10/2014
Molinia-dominated pasture	A	05/10/2014
Sedge-dominated pasture	A	10/10/2014
Rush-dominated pasture	B	22/09/2014
Heather	A	05/11/2014
Bracken	C	28/07/2015
Timothy/white clover	D	28/08/2015
Ryegrass/white clover	D	28/08/2015
Lucerne	D	28/08/2015
Reed canary	D	28/08/2015
Triticale	E	23/09/2015
Oats	E	23/09/2015
Winter rye	E	30/07/2015
Beet	E	09/11/2015
Maize	E	15/10/2015
Digestate	F	10/09/2015

[a] *A*: Insh Marshes Nature Reserve near Kingussie; *B*: Eastertown Farm near Crawfordjohn; *C*: Ben Lawers Nature Reserve near Killin; *D*: Boghall Farm near Edinburgh; *E*: Kirkton of Kinellar Farm near Aberdeen; *F*: Mains of Keithick Farm near Coupar Angus

$$\text{Organic solids} = (100 - \text{Ash\%})/100 \quad (1)$$

$$\text{NFE (nitrogen-free extract)} = 100 - (\text{Crude protein\%} + \text{Crude fibre\%} + \text{Ash\%} + \text{OilB\%}) \quad (2)$$

Further, subsamples of all the materials were sent to the Department of Chemistry, Aarhus University, Denmark where all the samples were milled to <1.0 mm particle size and then subjected to HTL. HTL batch reactions were carried out in duplicate in custom build Swagelok bomb-type reactors of 20 mL volume. The reactors were submerged completely into an OMEGA FSB-3 fluidised sand bath via a steel chain. The fluidised sand bath temperature was set to 350 °C. Once the desired residence time of 20 min (including heat up time) was reached, the reactor was quenched in a cold water bath. Once cold, the reactors were dried with compressed air, and any residual sand was removed. Each reactor was then weighed, and the produced gas vented before weighing again to determine the mass of gas gravimetrically by difference. The

Table 2 Parameters for biological methane potential calculation

	Digestibility (%)	Biogas yield L/kg organic solids	Methane in biogas (%)
Crude protein	65.1	700	71
Crude fibre	74.3	790	50
Oil B	67.5	1250	68
NFE[a]	70.0	790	50

[a] NFE is composed primarily of soluble sugars along with easily degradable polysaccharides such as starch and fructans, in addition to organic acids, pigments and resins

reactor contents, comprising of mostly water, solids and small amounts of bio-crude, were decanted into a 14-mL centrifuge tube. The reactor was rinsed with three aliquots of 3 mL dichloromethane (DCM) which were collected in a separate centrifuge tube. After centrifuging, the water was removed with a glass pipette and stored at 5 °C until further use. An aliquot of DCM was then used to wash the solids in the centrifuge tube, and the contents of both centrifuge tubes were subjected to vacuum filtration. The filter was rinsed with DCM until the DCM appeared clear. Finally, the DCM bio-crude extract was decanted into a pre-weighed brown glass bottle (30 mL). The DCM was evaporated under a stream of nitrogen. The filter paper was dried in an oven at 105 °C for 5 h and weighed to determine the mass of solids.

Total organic carbon (TOC) of the HTL water phase was measured using Hach Lange TOC analysis kits (LCK387). Total nitrogen (TN) was measured using the Hach Lange TN kits (LCK338). A total of 38 compounds in the water were analysed via GC-MS following derivatization using methyl chloroformate as described previously [7]. The bio-crude and grass samples were analysed for elemental composition using an Elementar CHNS-O Vario Macrocube elemental analyser. All samples were analysed in duplicate, and mean absolute errors for CHNS content were 0.3, 0.1, 0.04 and 0.01, respectively. The Dulong equation was used to calculate the higher heating values of the bio-crude and feedstock:

$$\mathrm{HHV}\left(\frac{\mathrm{MJ}}{\mathrm{kg}}\right) = 337\ \mathrm{C} + 1442\left(\mathrm{H}-\frac{\mathrm{O}}{\mathrm{H}}\right) + 93\ \mathrm{S} \tag{3}$$

5 mL of each replicate of the aqueous phase from HTL duplicate experiments was mixed and dried in an oven at 65 °C for 72 h until constant weight. The solid residue obtained was analysed for CHNS content as described above. A portion of the residue was also subjected to proximate analysis to determine the volatile and ash fractions by combustion in a furnace at 550 °C for 5 h. The results were used to calculate the theoretical production of methane and carbon dioxide using the Buswell equation [8]. The mass of sample obtained after water phase evaporation was too little to carry out full compositional analysis for calculation of theoretical biomethane potential using the above equation. Therefore, we used the Buswell equation, which bases biomethane composition on elemental composition:

$$C_cH_hO_oN_nS_s + \frac{1}{4}(4c-h-2o+3n+2s)\mathrm{H_2O} \rightarrow \frac{1}{8}(4c-h+2o+3n+s2)\mathrm{CO_2} + \frac{1}{8}(4c+h-2o-3n-2s)\mathrm{CH_4} + n\mathrm{NH_3} + s\mathrm{H_2}S \tag{4}$$

where c, h, o, n and s are the molar fractions of the solid residue. For the calculation of the methane yields, we applied a degradation factor of the volatile fraction of 0.6. This value is based on literature observations such as the COD removal rate of 60% for HTL aqueous phase, TOC removal rate of ~50% for pyrolysis aqueous liquor and hydrothermal carbonization aqueous phase COD removal rates of 80%, in references [9–11], respectively.

3 Results and discussion

Dry matter yields, moisture contents, ash content, ultimate analysis and higher heating value of the harvested materials are shown in Table 3. Crops currently used for energy production such as maize and winter rye exhibit the highest dry weight yield per hectare. Arable crop-derived biomass generally yielded more biomass, which is to be expected due to addition of fertiliser. However, possibly due to poorer growing conditions encountered in 2015, the yield of beet was lower than would be normally expected. The highest biomass yield from natural vegetation is found from heather followed by molinia-dominated grasslands. The yields are similar (~6 t DM/ha) to the pasture-derived biomass yields of beet, lucerne and ryegrass even though no fertilisers were used. This is a significant factor to consider as the application of N fertiliser at 150 kg/ha entails an energy penalty for fertiliser production of 8.7 GJ/ha [12]. The moisture content of harvested materials ranges from 50 to 90%; it is

Table 3 Analysis of biomass samples

Biomass	Yield (t DM/ha)	Moisture (%)	Ash (db %)	C	H	N	S	O*	C:N	HHV (MJ/kg)
Herb pasture	2.3	90.2	12.3	42.0	5.6	2.4	0.1	37.7	17.6	15.4
Bog myrtle	–	63.6	2.7	49.6	5.9	1.7	nd	40.2	29.6	18.0
Molinia pasture	5.9	77.2	10.9	42.6	5.5	1.8	nd	39.2	23.6	15.2
Sedge pasture	2.5	72.6	12.2	41.8	5.4	1.7	nd	38.9	25.3	14.8
Rush pasture	3.1	78.1	8.0	44.3	5.7	1.8	nd	40.2	24.7	16.0
Heather	6.8	68.2	1.8	50.1	6.5	0.9	nd	40.8	58.4	18.9
Bracken	1.1	75.0	6.1	44.8	6.4	1.2	0.1	41.4	38.9	16.9
Timothy/wclover	8.8	50.6	4.7	47.4	6.3	2.0	0.2	39.3	23.2	18.0
Ryegrass/wclover	5.7	69.8	4.9	43.7	6.7	0.9	0.1	43.8	49.6	16.4
Lucerne	5.8	79.0	6.4	44.8	6.5	1.2	0.1	41	37.0	17.1
Reed canary	10.8	69.1	7.5	45.0	6.5	2.5	0.2	38.4	18.1	17.6
Triticale	9.0	56.5	10.4	47.1	6.2	1.3	0.3	34.7	35.2	18.5
Oats	7.9	49.7	4.2	44.8	6.1	0.5	nd	44.3	86.1	15.8
Winter rye	17.5	57.6	4.3	44.6	6.3	0.7	0.1	44	62.8	16.2
Beet	6.1	76.0	3.6	44.8	6.1	0.4	0.1	45	107	15.9
Maize	15.0	83.9	2.4	42.7	6.3	0.6	nd	47.9	68.8	14.8
Digestate	–	77.1	6.6	43.5	6.0	1.4	0.1	42.4	30.6	15.7

*calculated by difference

common to carry out HTL on continuous pilot scale at 80% moisture, so addition of some water may be necessary for certain biomasses. The ash contents vary significantly for different vegetation materials from a low of 2.7 wt.% for bog myrtle to a maximum of ~12 wt.% for herb and sedge. The nitrogen analysis in Table 3 mainly reflects the protein content of the biomass; it is generally quite low, indicating maximum protein contents of around 15 wt.% (estimated via the N to protein conversion factor of 6.25).

Table 4 shows the methane potential of the different biomasses, the energy potential per tonne calculated using methane's heating value and the methane and energy production per hectare using data from Table 3. Materials derived from natural vegetation such as molinia grass, rush pasture and heather-dominated vegetation produced gross energy values, on a mass basis, comparable with that from grass pasture and crops. If harvesting of these crops can be performed in an energy efficient way, it would make them a suitable feedstock for AD. Generally, energy requirements for harvesting of perennial grasses such as switchgrass and reed canary grass are much lower than, e.g. maize. Switchgrass and reed canary mowing has been estimated to consume 0.33 and 0.14 GJ/ha, respectively, while maize grain harvest consumes 1.28 GJ/ha [13]. It also has to be considered that perennial grasses generally do not require tillage, seeding and crop management. Taking these into consideration, maize has been estimated to require 6.2 GJ/ha for operation of agricultural machinery from ploughing to harvest. Once switchgrass and reed canary are established, these crops only require 0.84 and 0.95 GJ/ha, respectively [13].

The crops currently used for anaerobic digestion, rye and maize yield around 10 GJ/t, similar to the majority of other biomasses. Taking the area specific yields of harvesting into account, the greatest methane productivity was from crops currently used commonly for AD, i.e. rye and maize. As mentioned previously, the yield from beet was lower than that normally obtained. However, the relatively high productivity from reed canary grass is notable. Of the natural vegetation types, heather- and molinia-dominated grasslands were the most productive with 70 and 55 GJ/ha, respectively. On average, the biomasses yield 71 GJ/ha which is comparable to the overall average in Ireland is estimated by Murphy et al. (2009) as 74.3 GJ/ha [14].

Gissén et al. (2014) estimated the energy output from hemp, beet, maize, triticale, grass/clover ley and wheat ranging from 78 to 160 GJ/ha. Maize yielded 107 and triticale 92 GJ/ha compared to 146 and 90 GJ/ha calculated in the current study [15]. In addition to the total theoretical potential methane productivity from the materials, Table 4 also shows values for the yields of methane calculated from soluble and readily degradable carbohydrate. This is the fraction that is most easily converted during anaerobic digestion to methane. Other fractions derived from lipid, protein and, particularly, fibre are less easily converted. The proportions converted from these constituents will be controlled by the specific conditions of anaerobic digestion. It is therefore likely that the actual amounts of methane produced by a working anaerobic digestion system, using a particular crop feedstock, will lie between the values for soluble carbohydrate-derived methane and total potential methane. Comparing the methane and

Table 4 Energy analysis via anaerobic digestion

Biomass	Methane potential (m^3/t DM)	Gross energy (GJ/t DM)	Methane production (m^3/ha)	Gross energy (GJ/ha)	Soluble carb. methane (m^3/t DM)	Gross energy sol. carb. (GJ/ha)
Herb pasture	NA	NA	NA	NA	NA	NA
Bog myrtle	NA	NA	NA	NA	NA	NA
Molinia pasture	261	9.3	1534	55	158	33
Sedge pasture	260	9.3	650	23	162	14
Rush pasture	268	9.6	831	30	155	17
Heather	289	10.4	1965	70	137	33
Bracken	278	10	306	11	142	6
Timothy/wclover	274	9.8	2417	87	154	48
Ryegrass/wclover	232	8.3	1324	48	181	37
Lucerne	276	9.9	1592	57	144	30
Reed canary	273	9.8	2957	106	157	61
Triticale	277	9.9	2493	90	204	66
Oats	282	10.1	2228	80	186	53
Rye	277	9.9	4847	174	169	106
Beet	274	9.8	1671	60	249	54
Maize	272	9.8	4080	146	180	97
Digestate	NA	NA	NA	NA	NA	NA

NA not available

energy yields calculated from the theoretical biomethane potential (TBMP) to experimental BMP from literature enables an estimation of the accuracy of the TBMP. Gissén et al., for example tested BMP of five crops including beet, maize, triticale and a grass/clover ley. They obtained BMP yields of 390, 340, 380 and 290 m^3 CH_4/t DM, respectively compared to 274, 272, 277 and 250 m^3 CH_4/t DM calculated in the current work [15].

Triolo et al. (2011) tested ten samples of grasses, maize and straw and compared BMP to TBMP and found a BMP of 270 to 440 m^3/t VS. Their TBMP, using a different equation than in the current work, overestimated the BMP with estimations of 443–466 m^3/t VS [16]. The algorithm used in the current work included a biodegradability factor to account for some of the differences in TBMP and BMP resulting in more realistic values compared to experimental BMP.

In a further study by the same authors, 57 herbaceous and non-herbaceous biomass samples were analysed for BMP. Reed canary, for example, yielded between 100 and 300 m^3 CH_4/t VS, similar to our estimation of 274 m^3/t DM. Maize yielded above 400, while sugar beet yielded around 440 m^3, higher than our calculated values of 272 and 274 m^3, respectively, indicating that our calculations may underestimate the actual BMP [17]. A further comparison to data published by Cropgen UK, states values for maize and beet, respectively, as 300–55 and 290 m^3/t VS, was closer to our calculated values [18]. These comparisons to literature values show that the estimations in TBMP and BMP can vary widely, and an accurate estimation is difficult for a biological system such as AD. A full scale digester is likely to achieve lower yields compared to BMP as these are generally seen as the upper limit of what is achievable in a continuous anaerobic digester [19].

In order to compare the energy potential of the bioenergy production technologies HTL and AD, HTL was carried out on the different biomasses and the digestate. The effect of homogeneous alkali catalyst (K_2CO_3) was assessed by comparing catalysed and non-catalysed HTL. The HTL yields, HHV of bio-crudes, energy yields per mass and area are presented in Table 5. The bio-crude yields from all biomasses are essentially similar with an average of 25 wt.%, a minimum of 20 wt.% and a maximum of 30 wt.%. At similar reaction conditions, Zhu et al. obtained comparable bio-crude yields from barley straw of ~30% [20], while a different study showed yields for miscanthus of 30% [5]. In our work, the addition of alkali did not have a clear effect on bio-crude yields, resulting in higher or lower yields for different samples. The operational parameters for HTL in terms of residence time and temperature were not optimised in the current study, and it is therefore expected that optimisation of reaction conditions would increase the observed yields to some extent as shown by Zhu et al. [20]. Process water recirculation and enhanced mixing of reactants in continuous systems are also expected to increase yields further as demonstrated in previous work [21]. Therefore, the current estimation of HTL energy potential is quite conservative. The HHV of the bio-crudes were determined to be in the range of around 30–

Table 5 Energy analysis via hydrothermal liquefaction

	HTL yield (daf %)				HHV bio-crude (MJ/kg)		Gross energy yield (GJ/t DM)		Gross energy (GJ/ha)	
Biomass	H_2O	±	K_2CO_3	±	H_2O	K_2CO_3	H_2O	K_2CO_3	H_2O	K_2CO_3
Herb pasture	26.6	1	24.1	1.9	34.7	27.1	7.6	5.4	17.5	12.4
Bog myrtle	21.6	0.9	23.1	3.7	32.2	29.4	5.9	6.3	–	–
Molinia pasture	22.2	3.3	26.3	4.3	34.7	25.8	6.5	5.7	38.2	33.7
Sedge pasture	22.8	5.7	19.4	2.3	32.7	34.2	7.3	5.5	18.2	13.8
Rush pasture	22.8	5.7	23.8	3.9	33.8	32.6	6.7	6.8	20.8	20.9
Heather	25.6	0.1	30.4	0	35.1	31.4	8.4	8.9	57.2	60.8
Bracken	20.8	0.9	24.2	1.4	34	35.1	6.5	7.7	7.1	8.5
Timothy/wclover	23.3	1.5	23.7	2.2	34.2	35.6	7.2	7.6	63.7	67
Ryegrass/wclover	22	0.5	24.5	1.8	34	33.7	6.8	7.5	38.8	42.8
Lucerne	28.9	0.2	30.1	0.2	35.8	35.5	9.2	9.5	53.2	55
Reed canary	26	1.1	24	3	32.6	34	7.7	7.4	83	79.7
Triticale	26.1	0.2	22.5	0.6	30	33.7	7.2	7	64.6	62.7
Oats	25.1	1	23.3	1.3	32.7	35.7	7.4	7.6	58.7	59.7
Rye	24.7	2.2	24.5	0.7	29.8	31.6	6.8	7.2	118.6	125.3
Beet	20.3	0.1	20.3	1.3	31.8	34.4	6.2	6.6	37.5	40.6
Maize	27.6	1.3	23.4	1.7	33.8	32.7	8.3	6.8	124	101.8

± mean absolute error, $n = 2$

35 MJ/kg. This represents a significant increase from the original energy density of around 15 MJ/kg (see Table 3). The yields of bio-crude from digestate were remarkably low with only 8 wt.%. This indicates that digestate is not suitable as a feedstock for HTL, at least when it is produced principally from rye as in the current study. Eboibi et al. (2015) were able to show that the liquefaction of digestate produced from cow manure led to much higher bio-crude yields in the range of 20–42 wt.% [22]. The reason for this is the suspected high amounts of undigested lignin in the digestate from rye. Lignin does not perform favourably during HTL for the production of bio-crude with yields reported as low as 3.9 wt.% [23].

In terms of energy output per mass, the highest values were achieved for lucerne and heather with around 9 GJ/t DM. The remaining vegetation types all exhibit a lower energy output from HTL than AD if the total theoretical methane potential is considered. If only the methane potential from easily digestible soluble carbohydrates is compared, the values of HTL are, on average, higher than those from AD. As a comparison, the energy yield using other technologies for liquid biofuel production has been estimated by the International Energy Agency (IEA) for agricultural residues: ethanol yields are reported as 2.3–5.7 GJ/t and fuel production via gasification to syngas with Fischer-Tropsch as 2.5–6.8 GJ/t [24]. It is evident

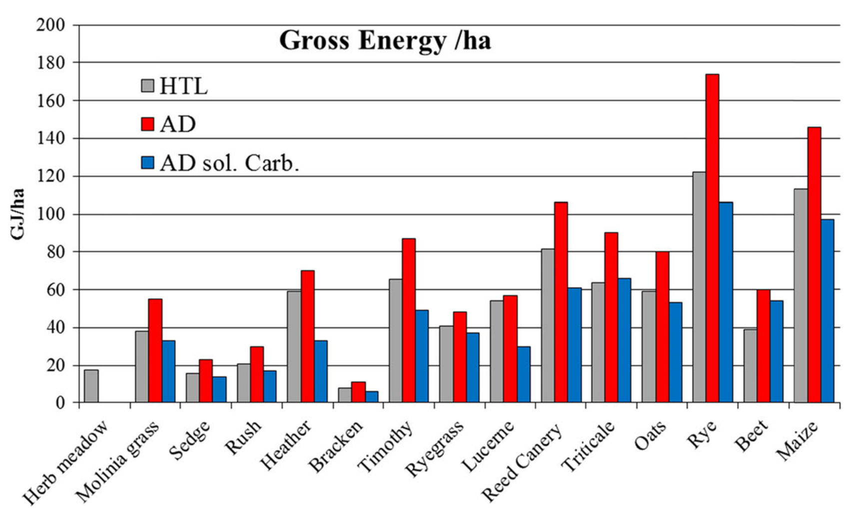

Fig. 1 Comparison of AD and HTL gross energy yield per hectare. AD sol. carb. represents the methane energy potential from solely the soluble carbohydrate fraction

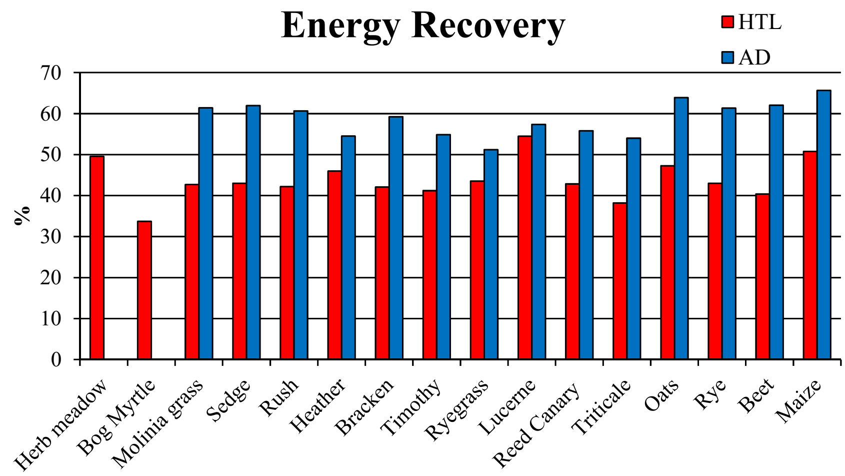

Fig. 2 Overall energy recovery comparison of AD to HTL

that even the higher end of the IEA estimates should be achievable using HTL. Molinia, bog myrtle and beet are the only crops, which do not achieve an energy yield of at least 6.8 GJ/t, and the lowest yield is found for bog myrtle at 6.3 MJ/t.

In terms of area specific energy yields, the crops commonly used for energy production to date, maize and rye, showed the highest energy output due to their high biomass yields.

Figure 1 compares the area specific energy output per area from AD to HTL. It is evident that the majority of crops have a higher energy yield via the AD route using the total methane potential calculations. The values for lucerne, heather and ryegrass are similar for both technologies with 5, 16 and 15% increased energy output for AD, respectively. The remaining samples are all shown to produce over 20% more energy via AD compared to HTL. The values for AD in Fig. 1 are similar to values stated by other researchers, e.g. 55.5 and 108 GJ/ha for wheat and grass in Ireland, respectively [14]. Comparing the HTL values to other technologies for the production of liquid fuels, the current results are quite promising. Adler et al. (2007) estimate an ethanol production from switchgrass of 70 and 49 GJ/ha for reed canary, while the current HTL assessment yielded an energy yield of 80 GJ/ha for reed canary. However, it has to be considered that the bio-crude generally requires upgrading via hydrotreatment to gasoline, diesel and kerosene, while ethanol production requires distillation. Although the hydrotreating step is potentially energy intensive, it does not entail a significant loss of chemical energy in the fuel, so that the GJ/ha numbers would not change significantly. If only the methane potential from the soluble carbohydrate fraction is considered, the energy output from HTL performs more favourably. All biomasses apart from triticale and beet yield, more energy per hectare via HTL compared to the energy from the soluble carbohydrate fraction via AD. As mentioned, a realistic assessment of the energy from AD most likely lies in between the total and soluble carbohydrate values.

In terms of total recovery of the available energy in the biomass samples, most biomasses perform quite similar as plotted in Fig. 2. The energy recoveries for AD are calculated based on the total theoretical methane potential (Table 4). The values from HTL are consistently lower compared to those from AD, on average by 15%. Lucerne shows the smallest difference with only 4% increased energy recovery. Beet shows the largest difference of 22% increased energy output from AD compared to HTL.

HTL energy recovery averages around 44%, but it has to be noted that the aqueous phase also contains significant amounts of energy, which could potentially be utilised to optimise

Table 6 Total organic carbon (TOC), total nitrogen (TN) and pH of the HTL water phases, with and without K_2CO_3

	H_20			K_2CO_3		
	TOC (g/L)	TN (mg/L)	pH	TOC (g/L)	TN (mg/L)	pH
Herb pasture	10.9	1090	5.2	16.1	1230	8.2
Bog myrtle	11.0	734	4.5	13.3	827	8.1
Molinia pasture	11.3	617	3.8	16.0	813	8.0
Sedge pasture	11.5	579	4.0	14.9	712	7.6
Rush pasture	10.5	613	3.8	17.2	331	7.9
Heather	11.0	249	3.6	15.2	315	7.2
Bracken	11.0	361	4.8	15.6	1220	7.9
Timothy	12.6	488	4.1	18.7	622	7.2
Ryegrass	11.6	339	3.6	16.0	576	6.9
Lucerne	14.4	616	5.3	16.9	1550	7.8
Reed canary	12.3	166	7.0	17.1	576	7.0
Triticale	12.0	129	3.4	18.5	660	6.1
Oats	11.5	219	3.6	17.7	337	7.1
Rye	11.8	120	3.3	19.6	227	5.9
Beet	11.0	248	3.6	18.5	316	6.2
Maize	12.7	510	4.0	18.5	668	7.1
Digestate	5.9	443	4.7	9.0	89	7.2

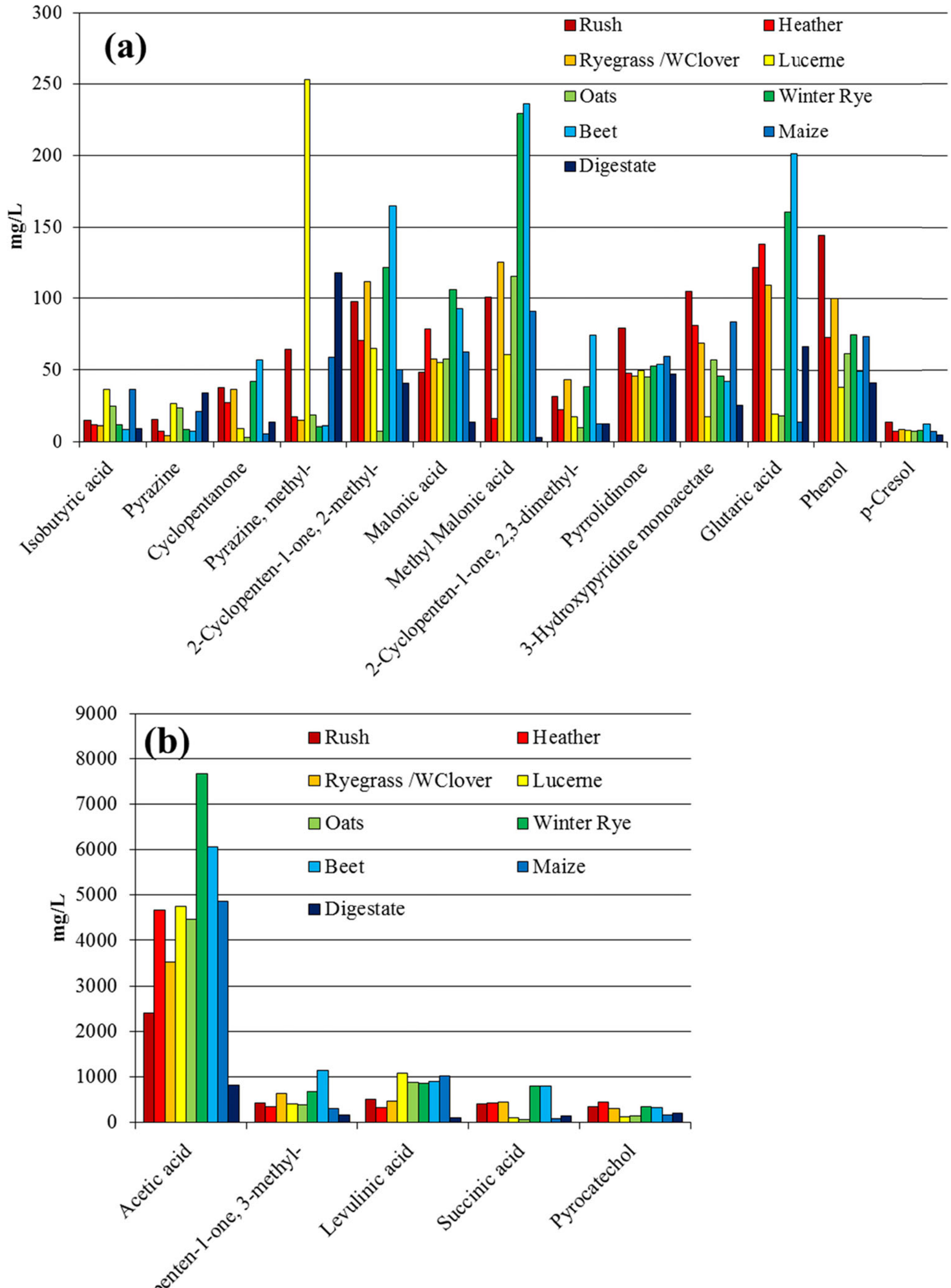

Fig. 3 **a**, **b** Concentration (mg/L) of selected compounds in the water phase from non-catalytic HTL. **a** Low concentrations. **b** High concentrations

energy recovery as discussed in the following sections. The anaerobic digestion energy recovery averages at 59%; however, the energy recovery in the more easily digestible soluble carbohydrate fraction is only 37%. The average for working AD system will most likely lie in between the values of 37 and 59% and could therefore potentially recover similar amounts of energy compared to the average of 44% for HTL.

The analysis of bulk parameters of the water phase post HTL is presented in Table 6 and includes TOC, TN and pH. The average energy recovery in the bio-crude was around 44% with a high of 55% for lucerne and a minimum of 34% for bog myrtle. Large amounts of the energy not found in the bio-crude are lost to the water phase as can be seen in the total organic carbon values shown in Table 6. TOC levels range from 10 to 20 g/L which represent approximately 20–35% of the carbon contained in the original biomass. On a mass basis, the water phase yield averages at 47% showing that a large fraction of the biomass is liquefied and found in the

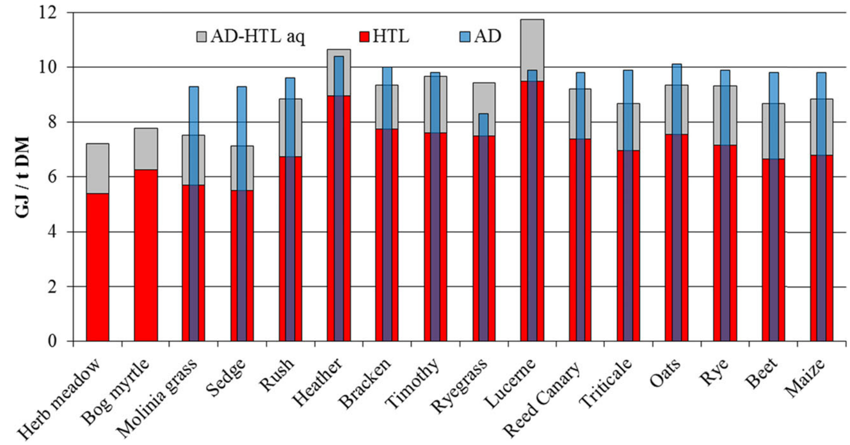

Fig. 4 Comparison of energy yields per mass of biomass via HTL (with K_2CO_3) and subsequent AD of the HTL water phase and direct AD of biomass

aqueous phase. Ideally, this energy should be recovered for optimisation of an integrated bioenergy system. AD of the HTL process water is an option which should therefore be considered. The use of catalyst resulted in considerably higher TOC and TN values in the water phase, due to higher degrees of liquefaction and reduced amount of solids and therefore carbon lost to the residue. The pH of the catalytic experiments is alkaline in most cases, while it is acidic when no catalyst was used. This should be taken into consideration when AD of the process waters is investigated. Typically, AD systems run at neutral conditions suggesting that the use of K_2CO_3 would yield a more suitable water phase. The nitrogen levels are low compared to the organic carbon levels, in the range of 130–1550 mg/L, while TOC levels are in the range of 10–20 g/L. This results in C:N ratios ranging from 100:1 to 1000:1. For the application of AD of the water phase, a C:N ratio of around 20–30:1 is ideal [19], indicating that the process water would have to be supplemented with a nitrogenous substrate such as abattoir waste. Alternatively, the HTL process could be supplemented with a feedstock high in nitrogen such as dried distillers grains with solubles, sewage sludge or manure. Previous work has shown that the water phase from HTL of DDGS results in C:N ratios of 3–5:1 [21], so mixing feedstocks is a promising route to obtain a suitable C:N ratio for AD of the HTL water phase.

The aqueous phase from HTL was additionally analysed via GC-MS to identify some of the major compounds present in high concentrations. Figure 3 shows the levels of some selected compounds in the aqueous phases processed without K_2CO_3. The highest levels of any detected compound are observed for acetic acid with levels as high as 7500 mg/L. Levulinic and succinic acids are also present in high concentrations of around 500–1000 mg/L. Overall, the majority of compounds identified in the water phase are carboxylic and dicarboxylic acids. These compounds are expected to be suitable for anaerobic digestion and conversion to methane via methanogenesis. However, there are also significant amounts of ketones present; 3-methyl-2-cyclopenten-1-one is found to average around 500 mg/L with a high of 1142 mg/L for beet. 2,3-dimethyl-2-cyclopenten-1-one and cyclopentanone are present in much lower concentrations in the range of around 10–70 mg/L. These compounds are recalcitrant during AD, meaning they are not broken down by microbes and do not contribute to methane production. The most abundant nitrogen-containing compounds in the water phase is 2-pyrrolidinone which has a fairly equal concentration in all biomass samples of around 50 mg/L. Methyl-pyrazine and pyrazine were quantified on average in concentrations of 16 and 63 mg/L. The presence of phenolics in the water phase could pose an issue in the aqueous phase from HTL if it should be used for further processing via AD. Phenol has previously been shown to introduce a lag phase during the AD of HTL waters [9]. In the current study, phenol was present in concentrations ranging from 40 to 140 mg/L and pyrocatechol in the range of 120–450 mg/L. Hubner and Mumme (2015) showed in their experimental investigation into the AD of the aqueous phase from pyrolysis that phenol and catechol were successfully degraded by AD microbes to below detection limit [10]. The starting concentration of phenol and catechol in their study was similar to the levels found the HTL aqueous phase in the current study. Therefore, we do not anticipate any major inhibition of AD by these compounds, although its assessment is beyond the scope of this study. Hubner and Mumme (2015) further showed an overall removal rate of TOC in pyrolysis aqueous phase of up to 50%. Tommaso et al. (2015) demonstrated a COD removal rate of 60% and Wirth et al. (2014) a COD removal from hydrothermal carbonisation (HTC) process water of up to 80% [11].

Due to these promising results in the literature concerning further utilisation of the process waters from HTC, HTL and pyrolysis through anaerobic digestion, the biomethane potential of the HTL process water from the current investigation was calculated. The calculation is based on the Buswell equation, and a conversion rate of 60% was assumed, based on the three studies mentioned above. The calculation of the methane potential of the HTL aqueous phase is a function of the total mass found post HTL in the water phase, its elemental composition, its volatile fraction, the CH_4:CO_2 fraction produced (calculated from Buswell) and the fraction of volatiles degraded (assumed 0.6). The results from these calculations are plotted in Fig. 4 as light grey bars stacked on the energy from HTL in the form of bio-crude. Additionally, this data is compared to energy output from AD directly of the biomass.

Generally, the energy output from AD of HTL process water was higher for the experiments carried out with the use of K_2CO_3 with an average of 1.9 GJ/t compared to 1.2 GJ/t. It can be seen that the energy output from the combination of HTL with AD is similar for most samples compared to only AD. Using a combination of HTL and subsequent AD of the HTL process water is shown to yield additional energy, the overall energy recovery from HTL + AD averages at 55%, while HTL on its own yields an average energy recovery of 45%. The water phase post HTL most likely does require some kind of further processing before disposal or application as a fertiliser. Whether AD is the chosen route to process HTL waters largely depends on economics. The additional infrastructure would have to be justified by the ~10% additional energy which can be recovered via AD post HTL.

4 Conclusion

Natural crops and forage grasses have largely been overlooked for bio-crude production via HTL, and the HTL technology has not previously been investigated as an alternative for such low-value biomass. The current paper shows that HTL is potentially a viable technology for the production of liquid biofuels from grasses and crops. Area and mass specific energy yields via HTL surpass those from, e.g. ethanol production or Fischer-Tropsch. Anaerobic digestion generally yields more energy than HTL but in the form of biogas which may be less desirable in certain scenarios where a liquid fuel is required. Energy yields via HTL are higher compared to the calculated energy from the soluble carbohydrate fraction produced from AD but not as high as the total energy production if protein, lipids and fibres are included. HTL of the digestate from winter rye was further shown not to be a viable option due to very low bio-crude yields. AD of the HTL process water on the other hand was able to produce around 10% additional energy and could be an option for the utilisation of HTL process waters.

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